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(54) Detergent compositions.

(57) A laundry detergent composition providing cleaning and softening of textiles comprises an anionic surfactant, a water soluble cationic compound which may be the salt of a mono C₁₀-C₁₄ alkyl primary, secondary or tertiary amine, or a water soluble mono C₁₀-C₁₄ alkyl quaternary ammonium compound and a smectite type clay. A detergent builder salt is a preferred component of the granular form of the composition which may contain other conventional detergent ingredients.

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DETERGENT COMPOSITIONS

Field of the Invention

This invention relates to detergent compositions that clean well and also act as textile softeners.

Background of the Invention

5 Numerous attempts have been made to formulate laundry detergent compositions that have both good cleaning properties and also textile softening properties so as to avoid the need to use a separate rinse-added textile softener product in addition to the usual laundry detergent. As
10 cleaning by definition involves the removal of material from the textile surface and as textile softening normally involves deposition of material onto the same surface, these attempts have necessarily required a compromise in formulation to be reached between cleaning and softening performance.

15 Furthermore, the most common commercially available organic textile softening compounds are cationic materials that are reactive towards the anionic surfactants used in conventional laundry detergents. If both types of material are formulated in a single product, they tend to interact on
20 addition to a wash liquor and, although in some instances the resulting complex has useful textile softening properties, its formation normally depresses the cleaning performance of the formulation and is therefore generally considered undesirable.

25 In order to overcome this problem, compositions have been proposed that have sought to minimise the mutual reactivity of the anionic and cationic materials

by the addition of compatibilising compounds such as the amido amines and fatty acids described in U.S. Patent Nos. 3,886,075 and 3,954,632. An alternative approach has been to incorporate one of the reactant materials in a form that inhibits its contact with the other in the wash liquor and examples of this type of formulation are taught in U.S. Patent Nos. 3,936,537 and 3,644,203. The performance of these compositions is however sensitive to the washing conditions that are employed.

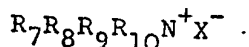
10 In an attempt to avoid the reactivity problem altogether, nonionic surfactants have been proposed in place of the conventional anionic surfactants and compositions of this type are described in e.g. British Patent Specification No. 1,079,388, German Auslegeschrift 1,220,956 and U.S. Patent No. 3,607,763. However it has been found that levels of nonionic surfactant sufficient to provide good cleaning 15 impair the softening of the cationic softener. Another proposal to provide acceptable cleaning and textile softening by avoiding the surfactant-softener interaction has been made in British Patent Specification No. 1,514,276 which 20 teaches the use of certain long chain tertiary amines that are nonionic in character at the wash liquor pH existing when a conventional laundry detergent is used. The commonly-assigned British Patent Application No. 11340 published 25 May 28, 1980 and British Patent Application No. 7923527 filed July 5, 1979 respectively also disclose cleaning and softening compositions comprising a combination of a long chain tertiary amine and a smectite-type clay in an anionic surfactant based detergent. The use of smectite- 30 type clays as softening agents in detergent compositions is taught in British Patent Specification No. 1,400,898. This type of softening agent does not affect the cleaning performance of the detergent composition but, if used on its own, requires a high level of incorporation for 35 effective softening performance possibly because the deposition of the clay on fabrics is not very efficient in the presence of anionic surfactants.

It has now been found that detergent compositions containing smectite-type clays and certain cationic compounds can be formulated which have cleaning performance equivalent to that of commercially available heavy duty laundry detergents together with textile softening performance that approaches that of rinse added fabric softeners.

Summary of the Invention

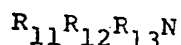
According to the present invention there is provided a detergent composition comprising

- 10 (a) 3%-40% of an anionic surfactant
- (b) 0.5%-15% of an organic nitrogenous compound capable of existing in cationic form in a 0.1% aqueous solution of pH 10 and selected from the group consisting of
- 15 (i) quaternary ammonium compounds of formula



wherein R_7 is C_8-C_{16} alkyl, each of R_8, R_9 and R_{10} is independently C_1-C_4 alkyl or hydroxy alkyl, benzyl, or $-(C_2H_4O)_xH$ where x has a value from 2 to 5, not more than one of R_8, R_9 or R_{10} being benzyl, and X is an anion,

- 20 (ii) aliphatic amines of general formula



wherein R_{11} is C_8-C_{18} alkyl, R_{12} and R_{13} are independently hydrogen, C_1-C_4 alkyl or hydroxyalkyl, benzyl, or $-(C_2H_4O)_xH$ where x has a value from 2 to 5, or the water soluble salts thereof; and

- 25 (c) from 1.5% to 45% by weight of the composition of an impalpable smectite-type clay having an ion exchange capacity of at least 50 meq per 100g,
- 30 provided that the molar ratio of component (b) to component (a) is less than 1:1.

Preferably component (b) is a $C_{12}-C_{14}$ alkyl tri C_1-C_4 alkyl or C_1-C_4 hydroxy alkyl ammonium salt and component (c) comprises a montmorillonite. In an especially preferred form of this embodiment component (b) is added to preformed spray dried detergent granules comprising components (a), (c) and also a detergent builder salt component (d).

Detailed Description of the Invention

In its broadest aspect the invention comprises three components, namely the anionic surfactant component (a), the the water soluble cationic component (b), and the smectite
5 type clay component (c).

The Anionic Surfactant

A wide range of anionic surfactants can be used in the compositions of the present invention.

Suitable anionic non-soap surfactants are water soluble
10 salts of alkyl benzene sulfonates, alkyl sulfates, alkyl polyethoxy ether sulfates, paraffin sulfonates, alphaolefin sulfonates, alpha-sulfocarboxylates and their esters, alkyl glyceryl ether sulfonates, fatty acid monoglyceride sulfates and sulfonates, alkyl phenol polyethoxy ether sulfates, 2-
15 acyloxy-alkane-1-sulfonates, and beta-alkyloxy alkane sulfonates. Soaps are also suitable anionic surfactants.

Especially preferred alkyl benzene sulfonates have about 9 to about 15 carbon atoms in a linear or branched alkyl chain, more especially about 11 to about 13 carbon
20 atoms. Suitable alkyl sulfates have about 10 to about 22 carbon atoms in the alkyl chain, more especially from about 12 to about 18 carbon atoms. Suitable alkyl polyethoxy ether sulfates have about 10 to about 18 carbon atoms in the alkyl chain and have an average of about 1 to about 12 -
25 $\text{CH}_2\text{CH}_2\text{O}-$ groups per molecule, especially about 10 to about 16 carbon atoms in the alkyl chain and an average of about 1 to about 6 $-\text{CH}_2\text{CH}_2\text{O}-$ groups per molecule.

Suitable paraffin sulfonates are essentially linear and contain from about 8 to about 24 carbon atoms, more especially
30 from about 14 to about 18 carbon atoms. Suitable alphaolefin sulfonates have about 10 to about 24 carbon atoms, more especially about 14 to about 16 carbon atoms; alphaolefin sulfonates can be made by reaction with sulfur trioxide followed by neutralization under conditions such
35 that any sultones present are hydrolyzed to the corres-

ponding hydroxy alkane sulfonates. Suitable alpha-sulfocarboxylates contain from about 6 to about 20 carbon atoms; included herein are not only the salts of alpha-sulfonated fatty acids but also their esters made from
5 alcohols containing about 1 to about 14 carbon atoms.

Suitable alkyl glyceryl ether sulfates are ethers of alcohols having about 10 to about 18 carbon atoms, more especially those derived from coconut oil and tallow.

Suitable alkyl phenol polyethoxy ether sulfates have about
10 8 to about 12 carbon atoms in the alkyl chain and an average of about 1 to about 6-CH₂CH₂O- groups per molecule. Suitable 2-acyloxy-alkane-1-sulfonates contain from about 2 to about 9 carbon atoms in the acyl group and about 9 to about 23
15 carbon atoms in the alkane moiety. Suitable beta-alkyloxy alkane sulfonates contain about 1 to about 3 carbon atoms in the alkyl group and about 8 to about 20 carbon atoms in the alkane moiety.

The alkyl chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as
20 coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium, or alkanol-ammonium cations; sodium is preferred. Mixtures of anionic surfactants are contemplated by this invention; a
25 satisfactory mixture contains alkyl benzene sulfonate having 11 to 13 carbon atoms in the alkyl group and alkyl sulfate having 12 to 18 carbon atoms in the alkyl group.

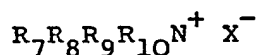
Suitable soaps contain about 8 to about 18 carbon atoms, more especially about 12 to about 18 carbon atoms.
30 Soaps can be made by direct saponification of natural fats and oils such as coconut oil, tallow and palm oil, or by the neutralization of free fatty acids obtained from either natural or synthetic sources. The soap cation can be alkali metal, ammonium or alkanol-ammonium; sodium is preferred.

35 The compositions contain from 3 to 40% of organic detergent, preferably from 4 to 15 of anionic detergent, more preferably 5-10% of anionic surfactant.

(b) The Water-Soluble Cationic Compound

The second essential component of the compositions of the present invention is an organic nitrogenous compound capable of existing in cationic form in a 0.1% aqueous solution at pH 10. This can be a compound of any of the following types;

(i) Quaternary ammonium compounds of formula



wherein R_7 is C_8-C_{16} alkyl, each of R_8, R_9 , and R_{10} is independently selected from C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_8, R_9 , and R_{10} should be benzyl.

The preferred alkyl chain length for R_7 is $C_{12}-C_{14}$ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohol synthesis. Preferred groups for

R_8, R_9 and R_{10} are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds are coconut trimethyl ammonium bromide

coconut methyl dihydroxyethyl ammonium bromide

decyl triethyl ammonium chloride

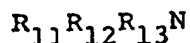
decyl dimethyl hydroxyethyl ammonium bromide

myristyl trimethyl ammonium methyl sulphate

lauryl dimethyl benzyl ammonium bromide

lauryl methyl (ethenoxy)₄ ammonium bromide

(ii) Aliphatic amines of general formula



wherein R_{11} is C_8-C_{14} alkyl, R_{12} and R_{13} are independently selected from hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl or $-(C_2H_4O)_xH$ where x has a value from 2 to 5, and the water soluble salts thereof.

Suitable amine salts can be the hydrohalide salts of primary, secondary, or tertiary amines, examples of such amines being:

Secondary Coconut methylamine
primary myristyl amine
lauryl dimethyl amine
lauryl diethyl amine
decyl dihydroxy ethyl amine
tallow dimethyl amine
secondary lauryl benzyl amine
Coconut dimethyl amine
dodecyl dipropyl amine

As stated previously, the compositions of the present invention combine good softening and cleaning performance and in order to maintain the latter it is essential that the overall surfactant character be anionic. The molar ratio of the cationic component (b) to the anionic surfactant component (a) should therefore be less than 1:1 and desirably should be less than 1:1.5. In preferred embodiments of the invention such as heavy duty laundry detergent formulations, the molar ratio should be less than 1:2.

Subject to these constraints the cationic compound will normally be present in an amount of from 0.5% to 15% by weight of the composition, preferably from 1% to 5% and most preferably from 1.5% to 3% by weight.

(c) The Smectite-Type Clay

The third component of the invention is a smectite-type clay having a particle size which cannot be perceived tactilely. Impalpable clays have particle sizes below about 50 microns; the clays used herein normally have a particle size range of from about 5 microns to about 50 microns.

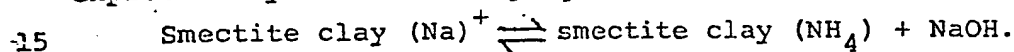
The clay minerals can be described as expandable, three-layer clays, i.e., aluminosilicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100 g. of clay and preferably at least 60 meq/100 g. of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

10 These are two distinct classes of smectite clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen atoms in the outer layers. The dioctahedral minerals are primarily trivalent
15 metal ion-based clays and are comprised of the prototype pyrophyllite and the members montmorillonite $(\text{OH})_4\text{Si}_4\text{--}$
 $\text{y}(\text{Al}_{4\text{--x}}\text{Mg}_x)\text{O}_{20}$, nontronite $(\text{OH})_4\text{Si}_{8\text{--y}}\text{Al}_y(\text{Al}_{4\text{--x}}\text{Fe}_x)\text{O}_{20}$, and
volchonskoite $(\text{OH})_4\text{Si}_{8\text{--y}}\text{Al}_y(\text{Al}_{4\text{--x}}\text{Cr}_x)\text{O}_{20}$, where x has a
value of from 0 to about 4.0 and y has a value of from 0 to
20 about 2.0. Of these only montmorillonites having exchange capacities greater than 50 meq/100 g. are suitable for the present invention and provide fabric softening softening benefits.

The trioctahedral minerals are primarily divalent metal
25 ion based and comprise the prototype talc and the members hectorite $(\text{OH})_4\text{Si}_{8\text{--y}}\text{Al}_y(\text{Mg}_{6\text{--x}}\text{Li}_x)\text{O}_{20}$, saponite $(\text{OH})_4\text{Si}_{8\text{--y}}\text{Al}_y(\text{Zn}_{6\text{--x}}\text{Al}_x)\text{O}_{20}$, vermiculite $(\text{OH})_4\text{Si}_{8\text{--y}}\text{Al}_y(\text{Mg}_{6\text{--x}}\text{Fe}_x)\text{O}_{20}$, wherein y has a value of 0 to about 6.0. Hectorite and saponite are the only minerals in this class that are of
30 value in the present invention, the fabric softening performance being related to the type of exchangeable cationic as well as to the exchange capacity. It is to be recognized that the range of the water of hydration in the above formulas can vary with the processing to which the clay has
35 been subjected. This is immaterial to the use of the smectite

clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure.

As noted hereinabove, the clays employed in the compositions of the present invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ions, and lithium ions. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation.



Since in the foregoing equilibrium reaction one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milli-equivalents per 100 g. of clay (meq/100 g).

The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971).

The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meq/100 g., and greater, for certain smectite clays. Illite clays although having a three layer structure, are of a non-expanding lattice type and have an ion exchange capacity

somewhere in the lower portion of the range, i.e., around 26 meq/100 g. for an average illite clay. Attapulgites, another class of clay minerals, have a spicular (i.e. needle-like) crystalline form with a low cation exchange capacity (25-30 meq/100 g.). Their structure is composed of chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms.

It has been determined that illite, attapulgite, and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the present compositions. However, the alkali metal montmorillonites, saponites, and hectorites, and certain alkaline earth metal varieties of these minerals such as calcium montmorillonites have been found to show useful fabric softening benefits when incorporated in the compositions in accordance with the present invention.

Specific non-limiting examples of such fabric softening smectite clay minerals are:

	<u>Sodium Montmorillonite</u>
20	Brock
	Volclay BC
	Gelwhite GP
	Thixo-Jel
	Ben-A-Gel
25	<u>Sodium Hectorite</u>
	Veegum F
	Laponite SP
	<u>Sodium Saponite</u>
	Barasym NAS 100
30	<u>Calcium Montmorillonite</u>
	Soft Clark
	Gelwhite L
	Imvite K
	<u>Lithium Hectorite</u>
35	Barasym LIH 200

Accordingly, smectite clays useful herein can be characterised as montmorillonite, hectorites, and saponite clay minerals having an ion exchange capacity of at least about 50 meq/100 g. and preferably at least 60 meq/100 g.

5 Most of the smectite clays useful in the compositions herein are commercially available under various trade names, for example, Thixogel No. 1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Imvite K from Industrial Mineral Ventures; Volclay BC and Volclay 325, from American Colloid
10 Co., Skokie Illinois; and Veegum F from R.T. Vanderbilt. It is to be recognised that such smectite minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

15 Within the classes of montmorillonites, hectorite and saponite clay minerals having a cation exchange capacity of at least about 50 meq/100 g., certain clays are preferred for fabric softening purposes. For example, Gelwhite GP is an extremely white form of smectite clay and is therefore
20 preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite clay mineral containing at least 3% of iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays
25 for use in detergent softening compositions. Imvite K is also very satisfactory.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14A x-ray diffraction pattern. This characteristic
30 exchange pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the compositions disclosed herein.

The smectite clay minerals useful in the present
35 invention are hydrophilic in nature, i.e., they display swelling characteristics in aqueous media.

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When used in compositions according to the invention, the smectite clay is present in an amount of from 1.5% to 45% by weight of the composition, preferably from about 2% to 15%, especially from about 5% to about 12%

5 Optional Ingredients

The detergent compositions of the present invention may of course include, as optional ingredients, components that are usually found in laundry detergents.

These include nonionic and zwitterionic surfactants, 10 builder salts, bleaching agents and organic precursors therefor, suds suppression agents, soil suspending and anti-redeposition agents, enzymes, optical brighteners, colouring agents and perfumes.

Nonionic and zwitterionic surfactants may be 15 incorporated in amounts of up to 50% by weight of the total surfactant but normally are present in amounts of less than 30% of the total surfactant. By 'total surfactant' is meant the sum of the anionic surfactant (a) cationic component (b) and any added nonionic and/or 20 zwitterionic surfactant. The incorporation of 15-25% nonionic surfactant based on the total surfactant weight (corresponding to 1-2% on a total composition basis) has been found to provide advantages in the removal of oily soils. Suitable nonionics are water soluble 25 ethoxylated materials of HLB 11.5-17.0 and include (but are not limited to) C_{10} - C_{20} primary and secondary alcohol ethoxylates and C_6 - C_{10} alkylphenol ethoxylates. C_{14} - C_{18} linear primary alcohols condensed with from seven to thirty moles of ethylene oxide per mole of 30 alcohol are preferred, examples being C_{14} - C_{15} (EO)₇, C_{16} - C_{18} (EO)₂₅ and especially C_{16} - C_{18} (EO)₁₁.

Suitable zwitterionic surfactants include the C_{12} - C_{16} alkyl betaines and sultaines. These and other zwitterionic and nonionic surfactants are disclosed in 35 Laughlin & Heuring USP 3,929,678.

Detergent builder salts are a preferred component (d) of the compositions of the invention and can be inorganic or organic in character. Non limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates, and silicates. Specific examples of such salts include the sodium and potassium tetraborates, bicarbonates, carbonates, tri-polyphosphates, pyrophosphates, penta-polyphosphates and hexametaphosphates. Sulphates are usually also present.

Examples of suitable organic alkaline detergency builder salts are:

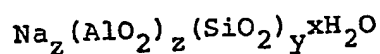
- (1) water-soluble amino polyacetates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates, N-(2-hydroxyethyl) nitrilotriacetates and diethylene triamine pentaacetates;
- (2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates;
- (3) water-soluble polyphosphonates, including sodium, potassium and lithium salts of methylenediphosphonic acid and the like and aminopolymethylene phosphonates such as ethylenediaminetetramethylene phosphonate and diethylene triaminepentamethylene phosphonate.
- (4) water-soluble polycarboxylates such as the salts of lactic acid, succinic acid, malonic acid, maleic acid, citric acid, carboxymethylsuccinic acid, 2-oxa-1,1,3-propane tricarboxylic acid, 1,1,2,2-ethane tetracarboxylic acid, mellitic acid and pyromellitic acid.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent No. 755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

Another type of detergency builder material useful in the present compositions and processes comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product. Such "seeded builder" compositions are fully disclosed in British Patent Specification No. 1,424,406.

Preferred water soluble builders are sodium tri-polyphosphate and sodium silicate, and usually both are present. In particular, it is preferred that a substantial proportion, for instance from 3% to 15% by weight of the composition of sodium silicate (solids) or ratio (weights ratio $\text{SiO}_2:\text{Na}_2\text{O}$) from 1:1 to 3.5:1 be employed.

A further class of detergency builder materials useful in the present invention are insoluble sodium alumino silicates, particularly those described in Belgian Patent 814,874 issued November 12, 1974 incorporated herein by reference. This patent discloses and claims detergent compositions containing sodium aluminosilicates of the formula



wherein z and y are integers equal to at least 6, the molar ratio of z to y is in the range of from 1.0:1 to about 0.5:1 and x is an integer from about 15 to about 264. A preferred material is $\text{Na}_{12}(\text{SiO}_2\text{AlO}_2)_{12} \cdot 27\text{H}_2\text{O}$. If present, incorporation of about 5% to 25% by weight of aluminosilicate is suitable, partially replacing water-soluble builder salts, provided that sufficient water-soluble alkaline salts remain to provide the specified pH of the composition in aqueous solution.

The detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

5 Bleaching agents useful in the compositions of the invention include sodium perborate, sodium percarbonate and other perhydrates at levels of from 5% to 35% by weight of the composition. Organic peroxy bleach precursors such as tetra acetyl ethylene diamine and tetra acetyl
10 glycouril can also be included and these and other precursors are disclosed in Belgian Patent No. 859461 published April 6th, 1978

 In compositions incorporating oxygen bleaches, bleach stabilisers are also preferred components usually
15 at levels of from 0.2% to 2% by weight of the composition. The stabilisers may be organic in nature such as the previously mentioned amino polyacetates and amino polyphosphonates or may be inorganic such as magnesium silicate. In the latter case the material may be added
20 to the formulation or formed in situ by the addition of a water-soluble magnesium salt to a slurried detergent mix containing an alkali metal silicate.

 Suds controlling agents are often present. These include suds boosting or suds stabilising agents such
25 as mono- or di-ethanolamides of fatty acids. More often in modern detergent compositions, suds suppressing agents are required. Soaps especially those having > 18 carbon atoms, or the corresponding fatty acids, can act as effective suds suppressors if included in the anionic
30 surfactant component of the present compositions. Usually about 1% to about 4% of such soap is effective as a suds suppressor. Very suitable soaps when suds suppression is a primary reason for their use, are those derived from Hyfac (C₁₈-C₂₂ hardened marine oil fatty acids available
35 from the Humko Corporation).

However, non-soap suds suppressors are preferred in synthetic detergent based compositions of the invention since soap or fatty acid tends to give rise to a characteristic odour in these compositions.

- 5 Preferred suds suppressors comprise silicones. In particular these may be employed a particulate suds suppressor comprising silicone and silanated silica releasably enclosed in water soluble or dispersible substantially non-surface active detergent impermeable
10 carrier. Suds suppressing agent of this sort are disclosed in British patent specification 1,407,997. A very suitable granular (prilled) suds suppressing product comprises 7% silica/silicone (15% by weight silanated silica, 85% silicone, obtained from Messrs.
15 Dow Corning), 65% sodium tripolyphosphate, 25% Tallow alcohol condensed with 25 molar proportions of ethylene oxide, and 3% moisture. The amount of silica/silicone suds suppressor employed depends upon the degree of suds suppression desired but it is often in the range
20 from 0.01% to 0.5% by weight of the detergent composition. Other suds suppressors which may be used are water insoluble, preferably microcrystalline, waxes having melting point in the range from 35 to 125°C and saponification value less than 100, as described in
25 British patent specification 1,492,938.

- Yet other suitable suds suppressing systems are mixtures of hydrocarbon oil, a hydrocarbon wax and hydrophobic silica as described in European patent application 782000035 and, especially, particulate
30 suds suppressing compositions comprising such mixtures, combined with a nonionic ethoxylate having hydrophilic lipophilic balance in the range from 14-19 and a compatibilising agent capable of forming inclusion compounds, such as urea. These particulate suds
35 suppressing compositions are described in European patent application No. 0008830.

Soil suspending agents are usually present at about 0.1 to 10%, such as water soluble salts of carboxymethyl cellulose, carboxyhydroxymethyl cellulose, polyethylene glycols of molecular weight from about
5 400 to 10000 and copolymers of methylvinylether and maleic anhydride or acid, available from the General Aniline and Film Corporation under the Trade Name Gantrez.

Proteolytic, amylolytic or lipolytic enzymes,
10 especially proteolytic, and optical brighteners, of anionic, cationic or nonionic types, especially the derivatives of sulphonated triazinyl diamino stilbene may be present. A further useful additive is a photo-
15 activated bleach comprising mixture of the tri- and tetra sulphonated derivatives of zinc phthalocyanine as described in B.P. Specification Nos. 1372035 and 1408144.

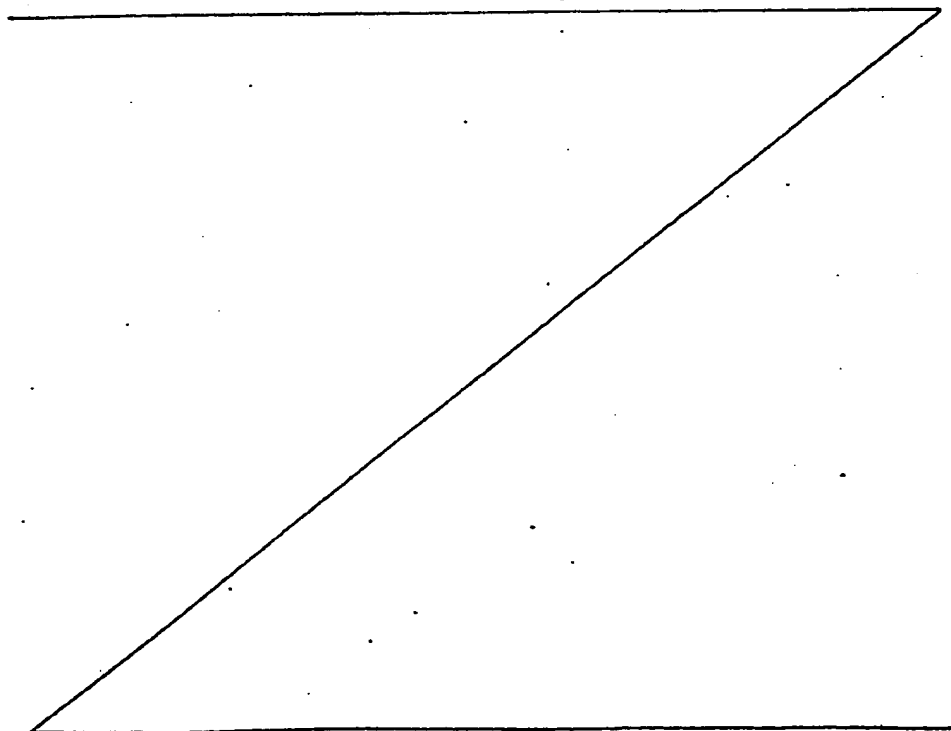
Colours, non-substantive, and perfumes, as required to improve the aesthetic acceptability of the product,
20 are usually incorporated.

Throughout the description herein where sodium salts have been referred to potassium, lithium or ammonium or amine salts may be used instead if their extra cost etc., are justified for special reasons.
25 Preparation of the Compositions

The detergent compositions may be prepared in any way, as appropriate to their physical form, as by mixing the components, co-agglomerating them or dispersing them in a liquid carrier. Preferably
30 the compositions are granular and incorporate a detergent builder salt and are prepared by spray drying an aqueous slurry of the non-heat-sensitive components, (a), (c) and the builder salt (d) to form spray dried granules into which may be admixed the

heat sensitive components such as persalts, enzymes, perfumes etc. The water soluble cationic (b) may be included in the slurry for spray drying, or it may be incorporated by dissolving or dispersing the cationic component in water or another suitable volatile liquid and then spraying this solution or dispersion onto the spray dried granules before or after other heat sensitive solids have been dry mixed with them. Alternatively the cationic component (b) can be dry mixed together with the other heat sensitive solids. The clay component may be added to the slurry for spray drying or may be dry mixed, as preferred for reasons unrelated to its softening effect, such as for optimum colour of the product.

The invention is illustrated by the following non-limiting examples.



Example 1

The following compositions were made up

		A	B
5	a) Sodium linear C ₁₂ alkyl benzene sulphonate	7.5	7.5
	a) Sodium tripolyphosphate	30.0	30.0
	a) Sodium Silicate (SiO ₂ Na ₂ O ratio 1.6:1)	5.0	5.5
	c) Sodium Perborate tetrahydrate	24.0	24.0
10	c) Mineral oil-hydrophobic silica - wax suds suppressor	0.2	0.2
	a) Sodium sulphate	14.0	12.0
	b) C ₁₂ -C ₁₄ alkyl trimethyl ammonium bromide	-	2.0
15	a) Sodium Montmorillonite clay	10.0	10.0
	a) Optical brightener	0.2	0.2
	c) Proteolytic Enzyme	0.3	0.3
	a) Moisture and miscellaneous	8.3	8.3
20	The compositions were made by first forming designated ingredients (a) into spray dried base granules. A concen- trated aqueous solution of the quaternary ammonium compound (b) was then made up and sprayed on to the base powder to give crisp free flowing granules into which were dry mixed		
25	the remaining ingredients (c).		
	The compositions were then used to wash 8lb soiled fabric loads in a Miele Model 422 Drum Automatic machine set to a prewash-mainwash cycle in which the mainwash was a boil wash. The water hardness was 14° Clark (Ca:Mg molar ratio		
30	2:1) and the product usage was 70g in the prewash and		

140 g in the mainwash. Artificially soiled cotton tracers and clean terry towelling tracers were added to each wash to permit evaluation of respectively, the cleaning and softening performance of the compositions. Following the wash
5 each load was air dried at ambient temperatures before being assessed by an expert panel. No differences in cleaning performance were apparent between either of the formulations but the softness assessment was as follows.

10 In a paired comparison between terry towelling tracers washed in compositions A and B using a Scheffe scale of assessment, composition B was rated better for softness than A by 1.62 panel score units with a least significant difference (LSD) of 0.39 psu at the 95% confidence level. A comparison
15 of the soiled swatches washed by each composition showed a slight advantage for composition B in soil removal, there being equivalence between the compositions on other soil stains.

It can thus be seen that composition B in accordance with the invention is superior in fabric softening performance to the prior art composition A whilst being equivalent to or slightly better than Composition A in cleaning
20 performance.

In this example the C₁₄ alkyl trimethyl quaternary component may be replaced by lauryl methyl dihydroxyethyl ammonium bromide, lauryl primary amine, C₁₂-C₁₄ alkyl
25 dimethyl amine, Coconut alkyl trimethyl ammonium bromide and N-tallowyl propylene diamine diacetate, whilst the sodium montmorillonite may be replaced by calcium montmorillonite, sodium hectorite or sodium saponite.

30 Examples 2-8

The following compositions are in accordance with the invention

	2	3	4	5	6	7	8
Sodium C ₁₂ linear alkyl benzene sulphate	8.0	6.0	2.0	4.0	8.0	-	12.0
Sodium tallow alkyl sulphate	-	-	-	4.0	-	-	-
5 Sodium tallow alkyl (EO) ₃ sulphate	-	-	-	2.0	-	4.0	-
Sodium C ₁₆ paraffin sulphonate	-	-	6.0	-	-	6.0	-
C ₁₄ -C ₁₅ linear primary alcohol (EO) ₇	-	-	-	-	2.0	-	-
10 C ₁₆ -C ₁₈ linear primary alcohol (EO) ₁₁	-	-	-	-	-	-	-
C ₁₁ -C ₁₅ linear secondary alcohol (EO) ₇	-	2.0	-	2.0	-	-	2.0
Coconut primary alcohol (EO) ₆	-	-	-	-	-	-	-
15 C ₁₂ -C ₁₄ trimethyl ammonium chloride	3.0	-	-	2.5	-	-	2.0
Coconut methylamine hydrochloride	-	2.0	-	-	-	-	-
C ₁₆ alkyl methyl dihydroxyethyl ammonium chloride	-	-	2.5	-	-	2.0	-
20 Coconut dimethylamine	-	-	-	-	2.0	-	-
Sodium montmorillonite clay	10.0	10.0	-	12.0	-	-	-
Calcium montmorillonite "	-	-	9.0	-	10.0	10.0	6.0
Sodium Hectorite "	-	-	-	-	-	-	10.0
Sodium Sulphate	12.0	6.0	1.5	12.0	6.8	3.0	10.0
25 Sodium tripolyphosphate	45.0	35.0	30.0	45.0	-	25.0	40.0
Sodium Carbonate	-	-	5.0	-	10.0	-	-
Sodium Silicate (SiO ₂ :Na ₂₀ ratio = 1.6:1)	10.0	6.0	10.0	6.0	6.0	6.0	7.5
Sodium Zeolite A	-	5.0	-	-	25.0	15.0	-
30 Sodium Perborate	-	20.0	25.0	-	20.0	20.0	-
Silica-Silicone suds suppressor	0.2	-	0.2	0.2	-	0.2	0.2

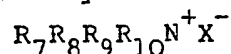
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	2	3	4	5	6	7	8
Hydrophobic silica - mineral oil -							
wax suds suppressor	-	0.2	-	-	0.2	-	-
Tetra sodium ethylene diamine							
5 tetra methylene phosphonate	0.2	0.5	-	0.5	1.0	-	0.5
Maleic anhydride - methyl vinyl							
ether copolymer	-	0.5	0.5	-	-	0.5	0.5
Stearic Acid	0.2	-	0.2	-	-	-	0.3
Tetrasulphonated zinc							
0 phthalocyanine	0.2	0.2	-	0.2	-	-	0.2
Optical Brightener	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Proteolytic Enzyme	0.3	-	0.3	0.3	-	0.3	-
Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Moisture and Miscellaneous	10.6	6.3	7.5	9.0	8.7	7.7	8.05

-1-

CLAIMS

1. A detergent composition comprising
 (a) 3%-40% of an anionic surfactant
 (b) 0.5%-15% of a nitrogenous organic compound capable
 5 of existing in cationic form in a 0.1% aqueous solution
 of pH 10 and selected from the group consisting of
 (i) quaternary ammonium compounds of formula



- 10 wherein R_7 is C_8-C_{16} alkyl, each of R_8 , R_9 and R_{10}
 is independently C_1-C_4 alkyl or hydroxy alkyl,
 benzyl, or $-(C_2H_4O)_xH$ where x has a value from 2
 to 5, not more than one of R_8 , R_9 or R_{10} being
 benzyl and X^- is an anion,

(ii) aliphatic amines of general formula



- wherein R_{11} is C_8-C_{18} alkyl, R_{12} and R_{13} are
 independently hydrogen, C_1-C_4 alkyl or hydroxy-
 alkyl, benzyl or $-(C_2H_4O)_xH$ where x has a value
 from 2 to 5, and water soluble salts thereof; and
 20 (c) from 1.5% to 45% by weight of the composition of
 an impalpable smectite-type clay having an ion exchange
 capacity of at least 50 meq per 100 g, provided that
 the molar ratio of component (b) to component (a) is
 less than 1:1.

- 25 2. A detergent composition according to Claim 1 wherein
 the molar ratio of (b):(a) is less than 1:2.

3. A detergent composition according to either one
 of Claims 1 and 2 wherein the water soluble cationic
 30 compound (b) is selected from quaternary ammonium
 salts in which R_7 is $C_{12}-C_{14}$ alkyl and R_8 , R_9 and R_{10}
 are selected from methyl and hydroxyethyl groups.

4. A detergent composition according to any one of Claims 1 to 3 wherein the smectite-type clay is a sodium or calcium montmorillonite clay.
5. A detergent composition according to any one of Claims 1 to 4 comprising from 5%-15% of component (a), from 1% to 5% of component (b), and from 2% to 15% of component (c).
6. A detergent composition according to any one of Claims 1 to 5 incorporating a further component (d) comprising from 10%-80% by weight of the composition of a detergent builder salt.
7. A granular detergent composition according to Claim 6 wherein component (b) is added to preformed granules comprising components (a) and (c) and (d).
- 15 8. A granular detergent composition according to Claim 7 wherein the preformed granules are spray dried.



European Patent
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EUROPEAN SEARCH REPORT

0026529

Application number

EP 80 20 0878.9

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,P	<u>EP - A1 - 0 011 340</u> (PROCTER & GAMBLE) * claims 1, 2, 6, 7 *	1,4,6, 8	C 11 D 1/62 C 11 D 1/40 C 11 D 3/30 C 11 D 3/12 D 06 M 13/46
	<u>DE - A1 - 2 648 304</u> (PROCTER & GAMBLE) EUROPEAN TECHNICAL CENTER) * claims 1 and 5; page 27, paragraph 2; page 28, paragraph 2 *	1	
A	<u>EP - A1 - 0 000 416</u> (PROCTER & GAMBLE) * complete document *		TECHNICAL FIELDS SEARCHED (Int. Cl.)
A	<u>US - A - 3 959 155</u> (R.E. MONTGOMERY et al.) * complete document *		C 11 D 1/00 C 11 D 3/00 D 06 M 13/00
A,P	<u>GB - A - 2 020 689</u> (COLGATE-PALMOLIVE) * complete document *		CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search Berlin		Date of completion of the search 01-12-1980	Examiner SCHULTZE